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Ab initio Quantum Chemical Reaction Kinetics: Recent Applications in Combustion Chemistry

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9th ICCK
June 28, 2015

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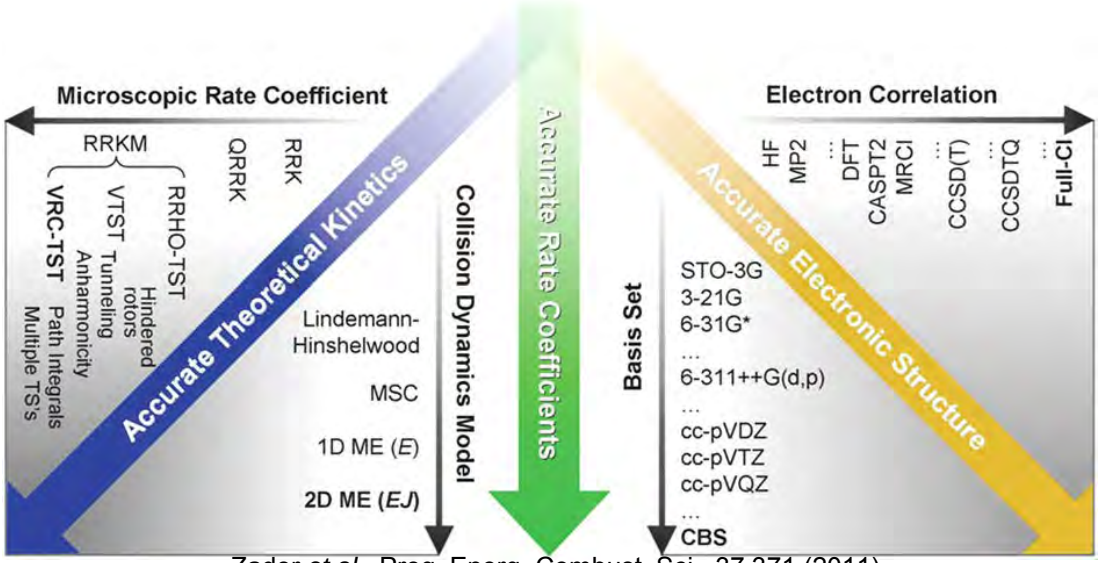
Why Quantum Chemical Reaction Kinetics Studies?

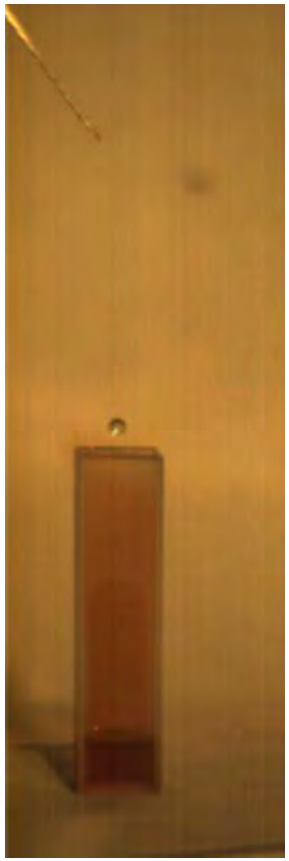
- Only Option When Experiments are not Possible or Limited
  - Combustion Conditions of P & T too Extreme to Probe
- Accuracy (E_a) can be as Good or Better Than Experiments
  - Thermochemical Accuracy Possible
  - Ideal for Branching Ratio Predictions for Closely Competing Reactions
- Can be a Cost Effective Alternate to Experiments
  - Hardware & Software Efficiencies Improving Constantly
- A Balanced Approach to Kinetics Calculations Recommended



Zador *et al.*, Prog. Energ. Combust. Sci., 37 371 (2011)

Our Interest in Combustion Chemistry

- Autoignition Chemistry
  - Low Temperature/Low Pressure Conditions
    - Bi-propellants



- Decomposition Chemistry
  - Emerging Energetic Materials
    - Explosives
    - Ionic Liquid Propellants

$N_2H_3 + NO_2$ Reaction Kinetics Perspective

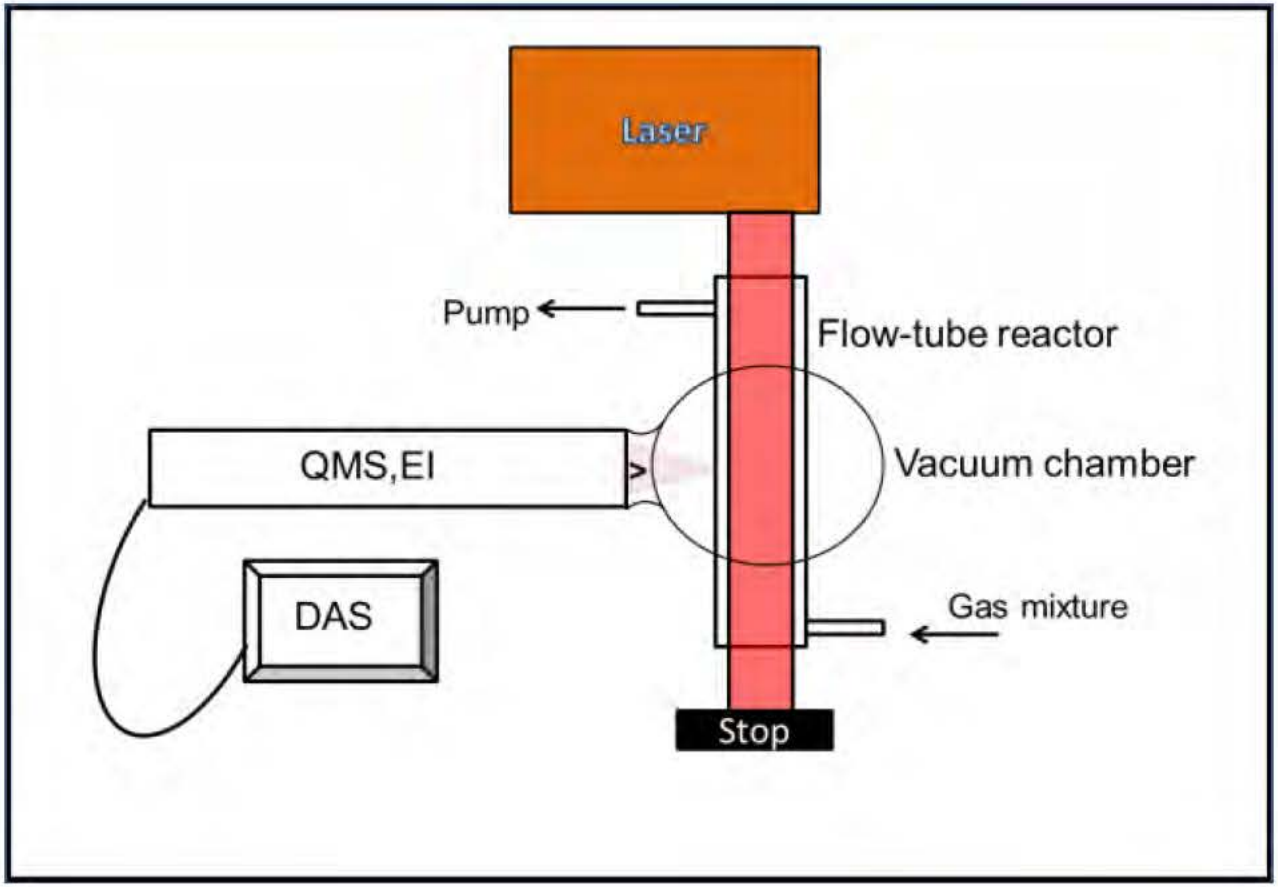
- Radical Chemistry Modelling
  - N_2H_4/NO_2 Autoignition
- Recent Works
  - Only Theoretical Studies
    - See Raghunath *et al.,* Adv. Quantum Chem., **69**, 253 (2014).....$k_{298\ K,\ 1atm} = (2.3 \times 10^{-11})$
    - See Daimon *et al.,* Sci. Tech. Energetic Materials, **74**, 17 (2013).....$k_{298\ K,\ 1atm} = (1.6 \times 10^{-14})$?
    - See Daimon *et al.,* J. Propul. Power, **30**, 707 (2014)..... $k_{298\ K,\ 1atm} = (1.9 \times 10^{-11})$
    - Also, See Kanno *et al.,* DOI: 10.1021/acs.jpca.5b00987 (2015)

      $CH_3NNH_2 + NO_2 \rightarrow$ Products, $k = (2.2 \times 10^{-13})$

      trans-$CH_3NHNH + NO_2 \rightarrow$ Products $k = (1.4 \times 10^{-12})$

      cis-$CH_3NHNH + NO_2 \rightarrow$ Products $k = (1.2 \times 10^{-12})$ $cm^3\ molecule^{-1}\ s^{-1}$
- This work
  - Pulsed Laser Photolysis - Flow Tube MS Experiments
    - First Experimental Determination
  - *Ab initio* Chemical Kinetics
    - Multi-reference Second-order Perturbation and Coupled-cluster Methods: PES (Potential Energy Surface)
    - RRKM (Rice–Ramsperger–Kassel–Marcus) Theory and Master Equation Simulations: k

Pulsed Laser Photolysis Flow Tube Apparatus



N_2H_3 Source & Flow Tube Chemistry

$N_2H_4 + h\nu \rightarrow N_2H_3 + H$	$\sigma_{193\ nm} = 450 \times 10^{-20}\ cm^2\ molec^{-1}$	1
$NO_2 + H \rightarrow NO + OH$	$k_2 = 1.3 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$	2
$N_2H_4 + H \rightarrow N_2H_3 + H_2$	$k_3 = 1.4 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$	3
$N_2H_4 + OH \rightarrow N_2H_3 + H_2O$	$k_4 = 3.6 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$	4
$N_2H_3 + NO_2 \rightarrow N_2H_2 + HONO$	k_5	5
$N_2H_3 + NO_2 \rightarrow$ other products	k_6	6
$HONO \rightarrow$ loss	$k_7 = 1\ s^{-1}$	7
$N_2H_3 \rightarrow$ loss	$k_8 = 10\ s^{-1}$	8
$H \rightarrow$ loss	$k_9 = 10\ s^{-1}$	9
$OH \rightarrow$ loss	$k_{10} = 10\ s^{-1}$	10

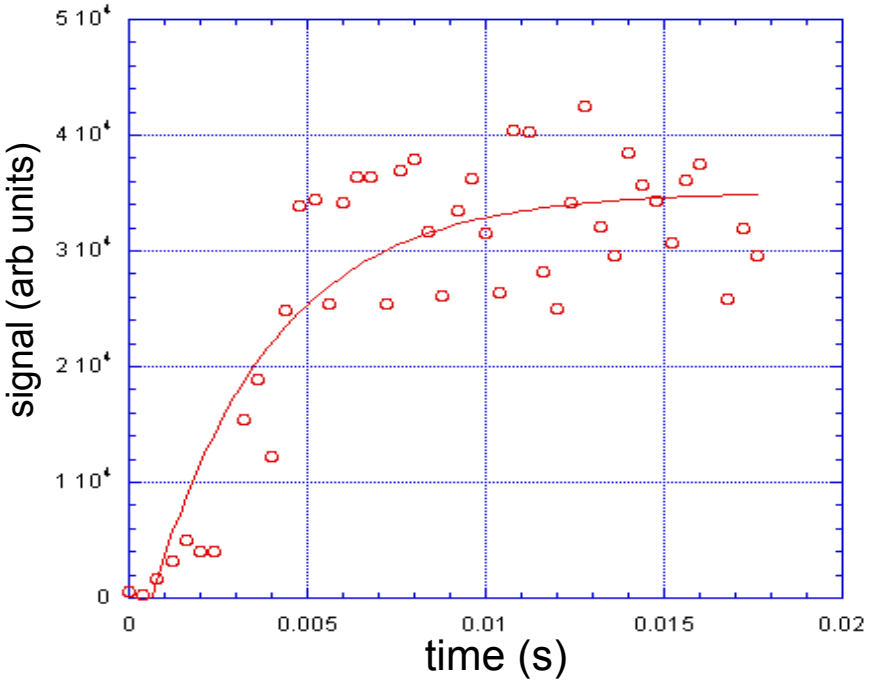
$$[HONO] = (k_5[NO_2][N_2H_3]_o)\{e^{-k_7.t} - e^{-k'.t}\}/(k' - k_7)$$

$$k' = (k_5 + k_6)[NO_2] + k_8$$

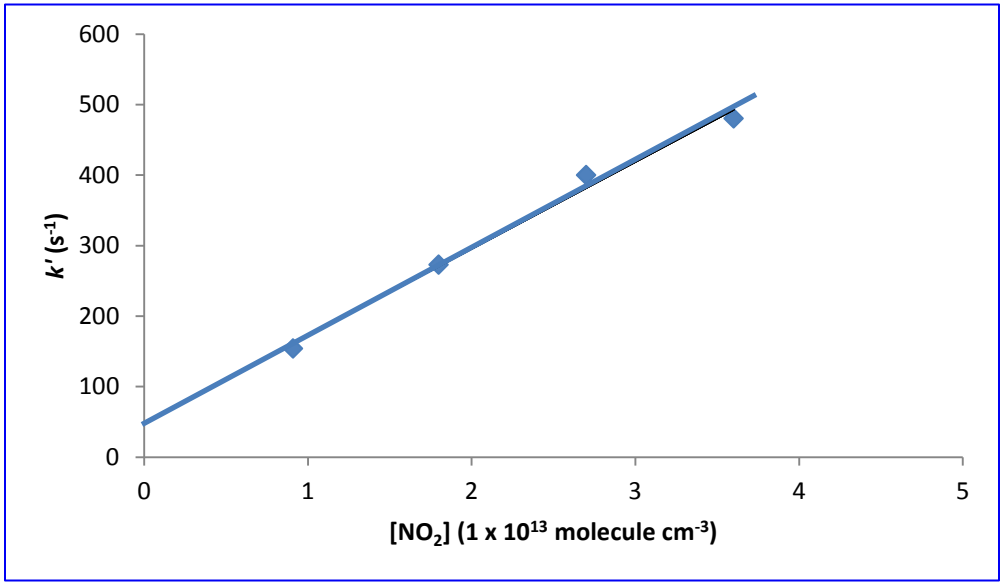
$[N_2H_4] = 5 \times 10^{14}$, $[H] = 5 \times 10^{12}$, $[NO_2] = 1 \times 10^{13}$ to 5×10^{13} molecule cm^{-3}

$N_2H_3 + NO_2$ Reaction Kinetics

Typical [HONO] Temporal Profile

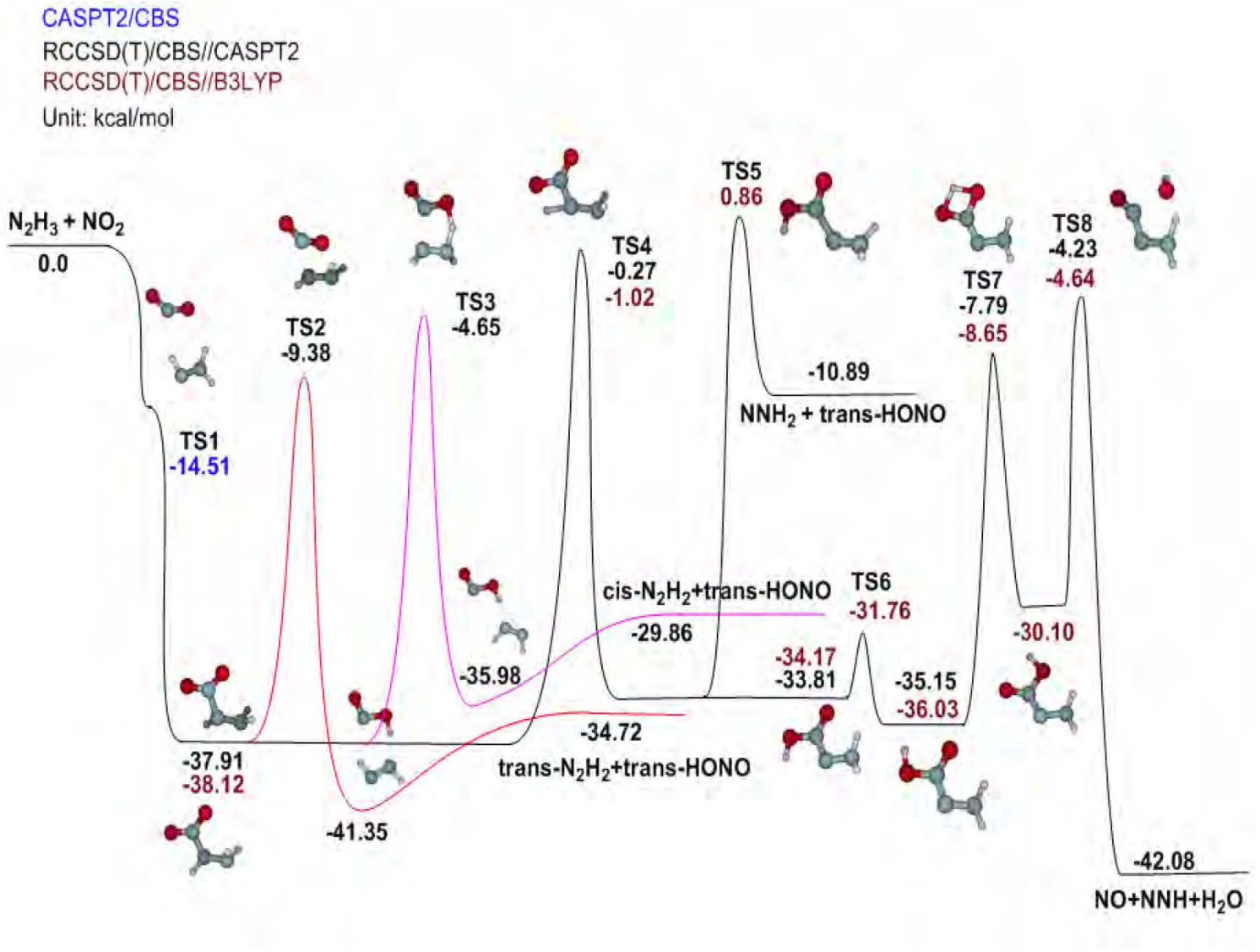


Second-order Plot

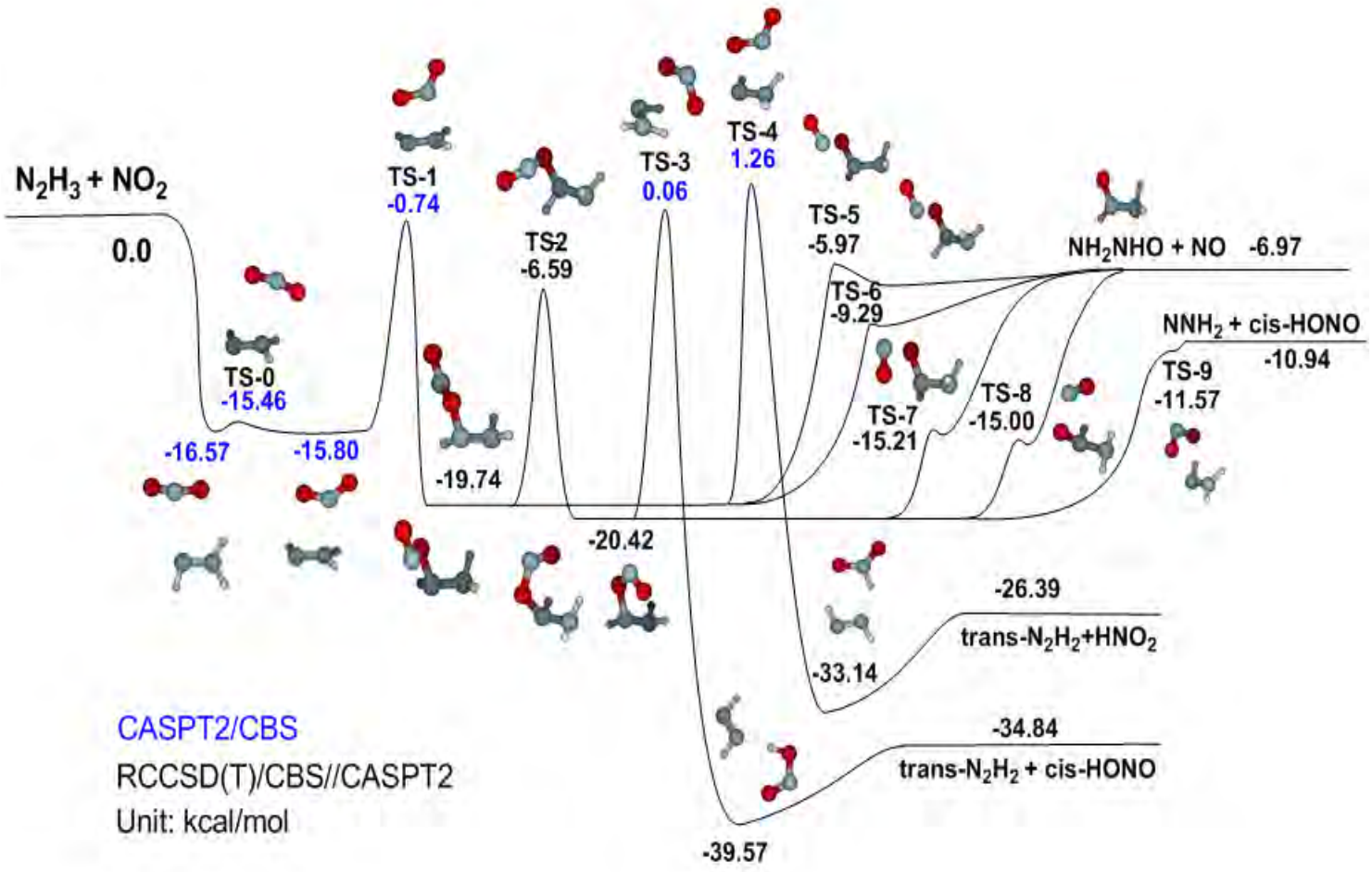


$k_{298\ K,\ 2\ Torr\ N_2} = (1.23 \pm 0.25) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$

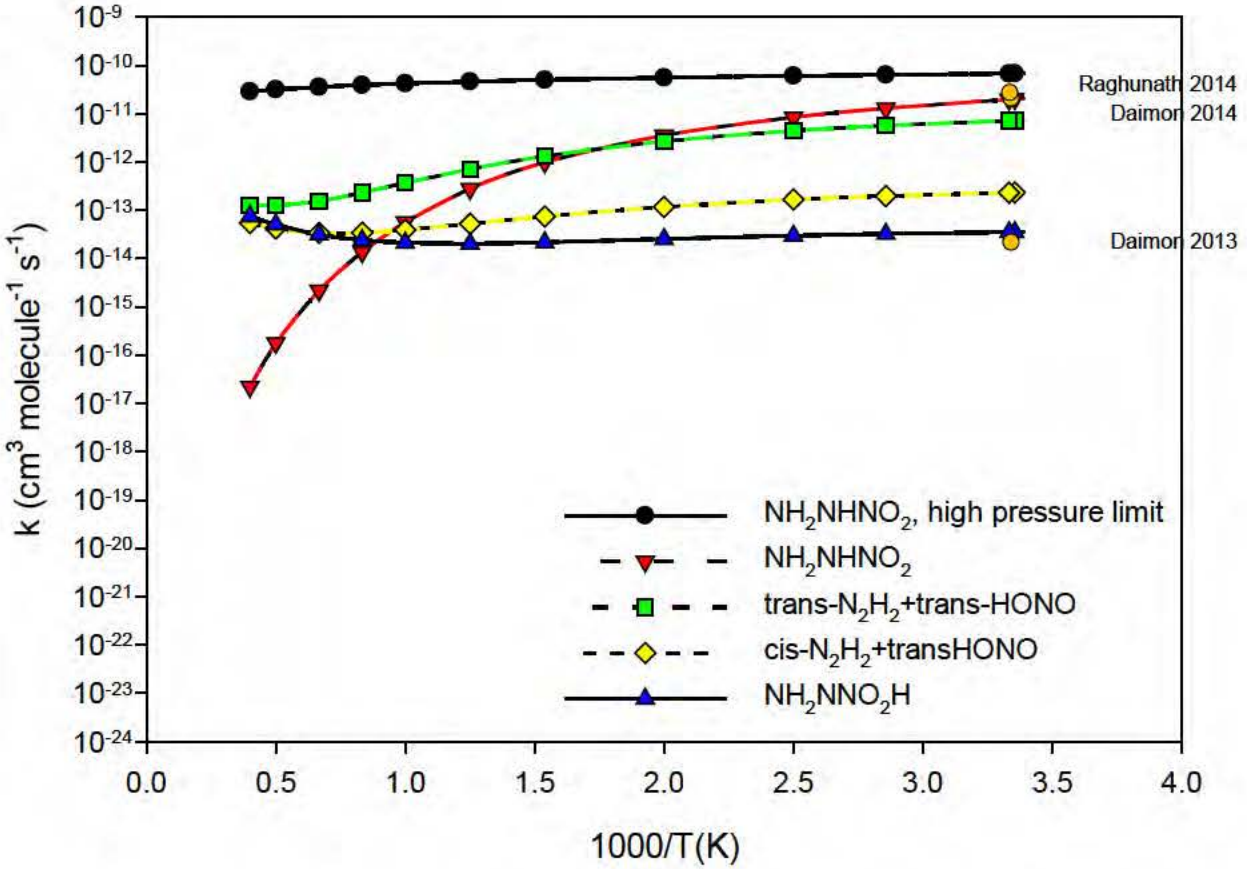
Potential Energy Surface for $N_2H_3NO_2$ Adduct Formation



Potential Energy Surface for N_2H_3ONO Adduct Formation

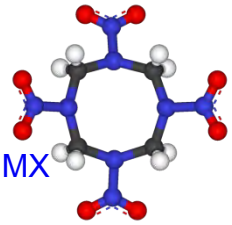


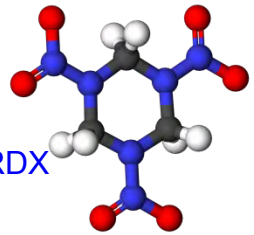
Branching Rate Coefficients (2 Atm N_2) & High Pressure Limit Versus T



MNB & DNB Energetic Materials Perspective

- MNB & DNB
  - Mononitrobiuret & 1,5-dinitrobiuret (less stable)
    - promising explosives

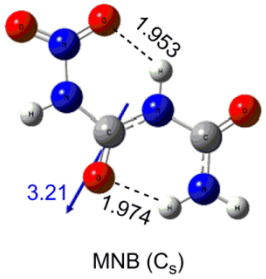




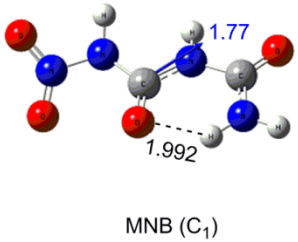
- Recent Works
  - See Geith *et al.,* Propellants, Explosives, Pyrotechnics, **29**, 3 (2004)
    - ΔH_{comb}(DNB) = (5195 ± 300) kJ kg^{-1} (bomb calorimetry and MP2/cc-pVTZ ΔH_f) cf HMX 9435 & RDX 9560 kJ kg^{-1}
    - V_d = 8660 ms^{-1}, cf HMX 9100 & RDX 8750 ms^{-1}
  - See Geith *et al.,* Combust and Flame, **139**, 358 (2004)
    - Recent synthesis (known since 1898 by Thiele) & decomposition mechanism studies
    - Initially NH_2NO_2 released, followed by residues decomposing to give HNCO
  - See Liu *et al.,* J. Phys. Chem. A **115**, 8064 (2011) & Sun *et al.,* J. Phys. Chem. A **118**, 2228 (2013)
    - Quasi-classical direct dynamics trajectory simulations to understand DNB decomposition
    - Elimination of HNN(O)OH intermediate identified
  - See Suntsova *et al.,* Struct. Chem., **24**, 745 (2013)
    - Electronic structure of DNB was studied by two-dimensional B3LYP potential energy scans
    - Solid- and gas-phase conformers differ

- This work
  - PESs for the thermal decomposition of MNB and DNB investigated
  - Temperature and pressure-dependent rate coefficients were calculated using micro-canonical transition state theory with master equation simulations

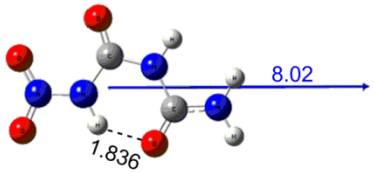
MNB & DNB Structures (M06-2X/aug-cc-pVTZ level)



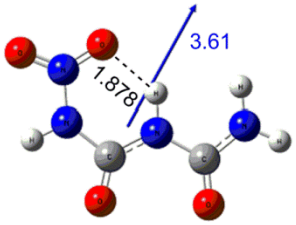
MNB (C_s)



MNB (C_1)



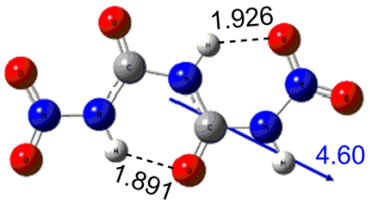
MNB (trans)



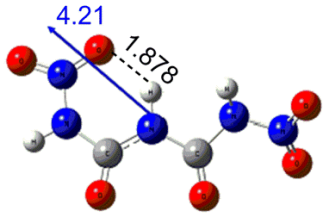
MNB (cis)

- H-bond Stabilized Conformers
  - MNB(C_s) 0
  - MNB(trans) +4.82
  - MNB(C_1) +6.38
  - MNB(cis) +7.95 kcal/mol

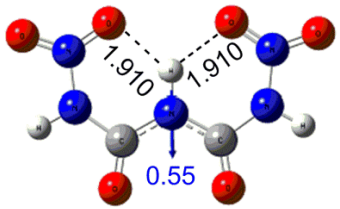
- Double H-bond Stabilized Conformers
  - DNB(C_s) 0
  - DNB(C_{2v}) +1.22
  - DNB(C_1) +7.82 kcal/mol



DNB (C_s)



DNB (C_1)



DNB (C_{2v})

Stationary Point Energies for MNB Thermal Decomposition

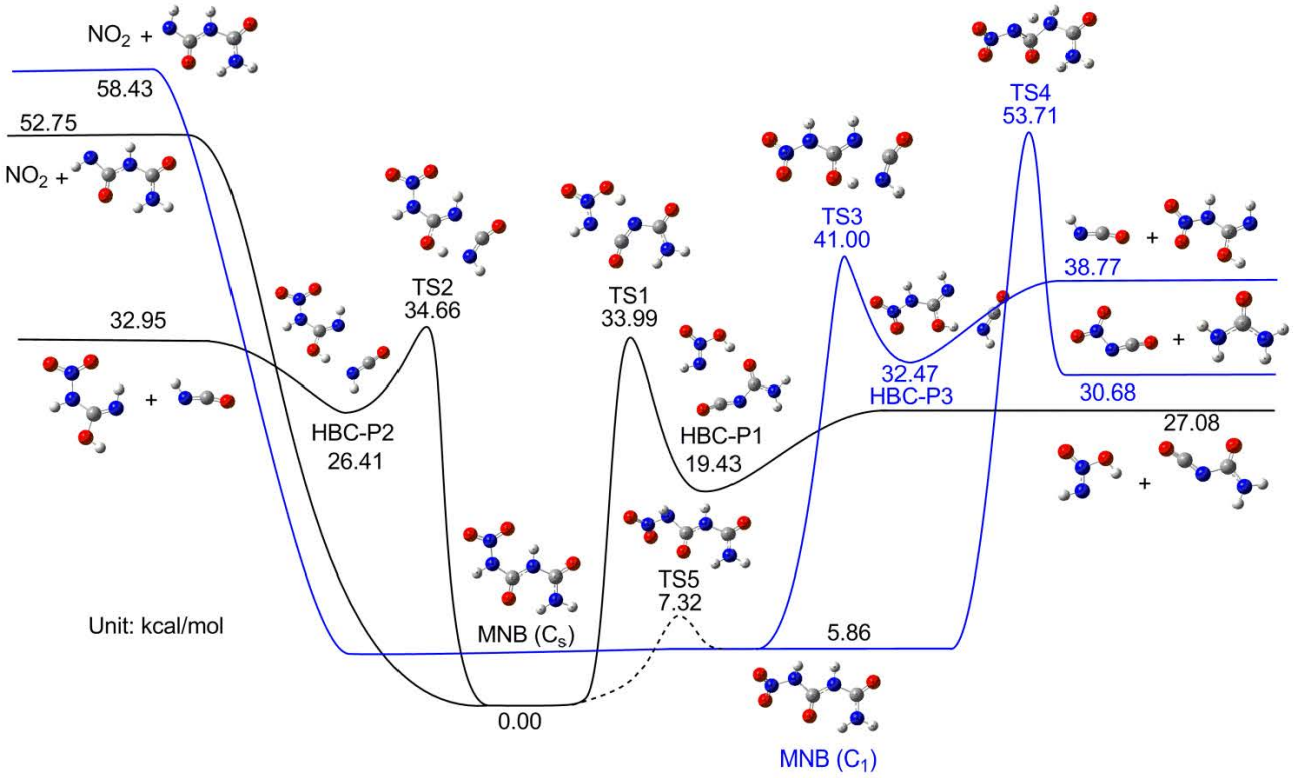
Species	M06-2X /aug-cc-pVDZ	M06-2X /aug-cc-pVTZ	RCCSD(T)/cc-pV∞Z //M06-2X/aug-cc-pVTZ
MNB (C_s)	0.00	0.00	0.00
TS1	33.86	33.18	33.99
HBC-P1	18.50	20.51	19.43
IM1 + HNN(O)OH	29.42	26.85	27.08
TS2	34.58	33.73	34.66
HBC-P2	27.75	26.20	26.41
IM2 + HNCO	30.43	32.17	32.95
trans-biuret radical + NO_2	51.41	51.34	52.75
MNB (C_1)	6.41	6.38	5.86
TS3	41.05	40.35	41.00
HBC-P3	34.23	32.65	32.47
IM3 + HNCO	40.33	38.46	38.77
TS4	53.77	54.71	53.71
$NH_2C(O)NH_2$ + NO,NCO	34.38	32.53	30.68
iso-trans-biuret radical + NO_2	57.25	56.99	58.43
TS5	7.84	8.29	7.32

All energies include zero-point corrections and are in kcal/mol relative to the global energy minimum of MNB (C_s).

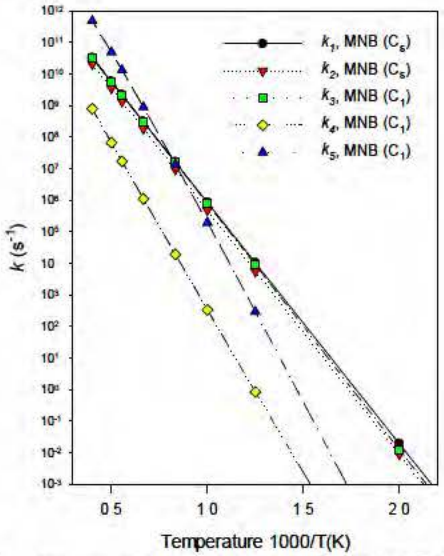
Within 1.0 kcal/mol for the barrier heights, and 1.8 kcal/mol for endothermicities compared to RCCSD(T)/cc-pV∞Z//M06-2X/aug-cc-pVTZ, implying that the M06-2X/aug-cc-pVTZ energies are good for larger analogous systems.

Potential Energy Surface for MNB Decomposition

RCCSD(T)/cc-pV∞Z//M06-2X/aug-cc-pVTZ



Ab initio Kinetics of MNB Thermal Decomposition

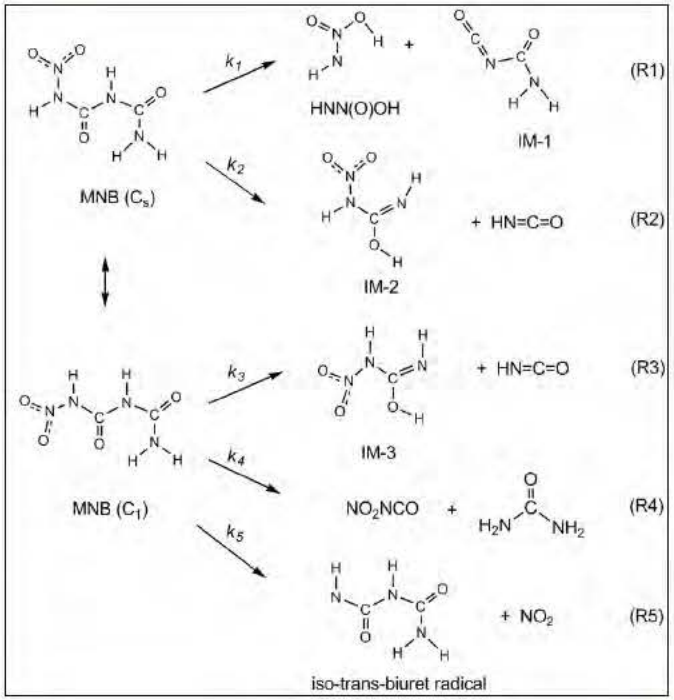


High-pressure rate limit for MNB (C_s) and MNB (C_1) primary thermal decomposition channels

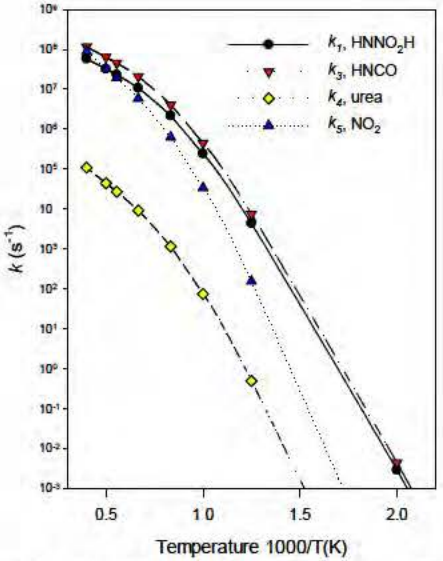
$k_{1,\infty} = 1.32 \times 10^{13}\, T^{0.131} \exp(-17474.7/T)$
$k_{2,\infty} = 1.05 \times 10^{13}\, T^{0.112} \exp(-17692.1/T)$
$k_{3,\infty} = 1.15 \times 10^{14}\, T^{-0.117} \exp(-18011.4/T)$
$k_{4,\infty} = 1.26 \times 10^{4}\, T^{2.539} \exp(-21375.5/T)$
$k_{5,\infty} = 2.07 \times 10^{23}\, T^{-2.002} \exp(-27714.8/T)$

Below 1200 K, HNCO & HNN(O)OH eliminations dominate, consistent with experimental work of Gieth *et al.* 2004

Above 1200 K, NO_2 elimination dominates



MNB (C_s) and MNB (C_1) primary thermal decomposition channels



Rate coefficients at pressure of 1 atm for MNB (C_s) and MNB (C_1) primary thermal decomposition channels

Pressure dependence of unimolecular decomposition evaluated using $\Delta E_{down} = 200 \times (T/300)^{0.85}$ cm^{-1} energy transfer probability model

Strong pressure dependences observed

HNCO & HNN(O)OH eliminations are competitive & dominate below 2500 K

NO_2 elimination becomes competitive only above 2500 K

R2 & R3 (HNCO) & R1 (HNN(O)OH) are primary (product) channels at ignition temperatures

Stationary Point Energies for DNB Thermal Decomposition

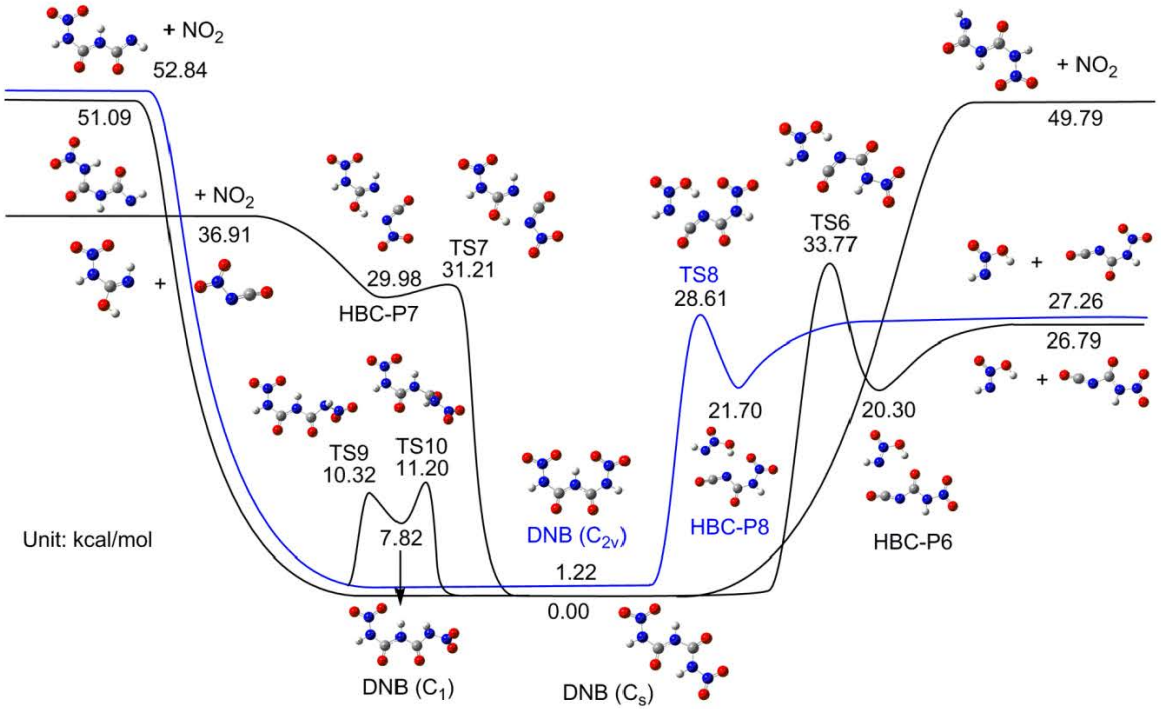
Species	M06-2X/aug-cc-pVDZ	M06-2X/aug-cc-pVTZ
DNB (C_s)	0.00	0.00
TS6	34.17	33.77
HBC-P6	21.58	20.30
HNN(O)OH + NO_2NHC(O)NCO	28.68	26.79
TS7	31.72	31.21
HBC-P7	30.70	29.98
IM2 + NO_2NCO	34.79	36.91
C_1-MNB radical + NO_2	50.20	49.79
trans-MNB radical + NO_2	50.89	51.09
DNB (C_{2v})	1.16	1.22
TS8	28.64	28.61
HBC-P8	22.35	21.70
HNN(O)OH + iso-NO_2NHC(O)NCO	29.08	27.26
cis-MNB radical + NO_2	52.54	52.84
DNB (C_1)	7.45	7.82
TS9	9.42	10.32
TS10	10.79	11.20

All energies include zero-point corrections and are in kcal/mol relative to the global energy minimum of DNB (C_s).

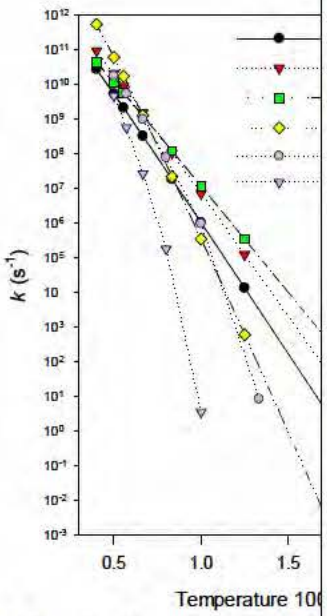
Predicted energy barrier heights from these two levels of calculation show excellent agreement, but discrepancy reaches to 2.1 kcal/mol for reaction endothermicities. Consequently, the M06-2X/aug-cc-pVTZ energies were used for carrying out the kinetics analysis for DNB decomposition.

Potential Energy Surface for DNB Decomposition

M06-2X/aug-cc-pVTZ

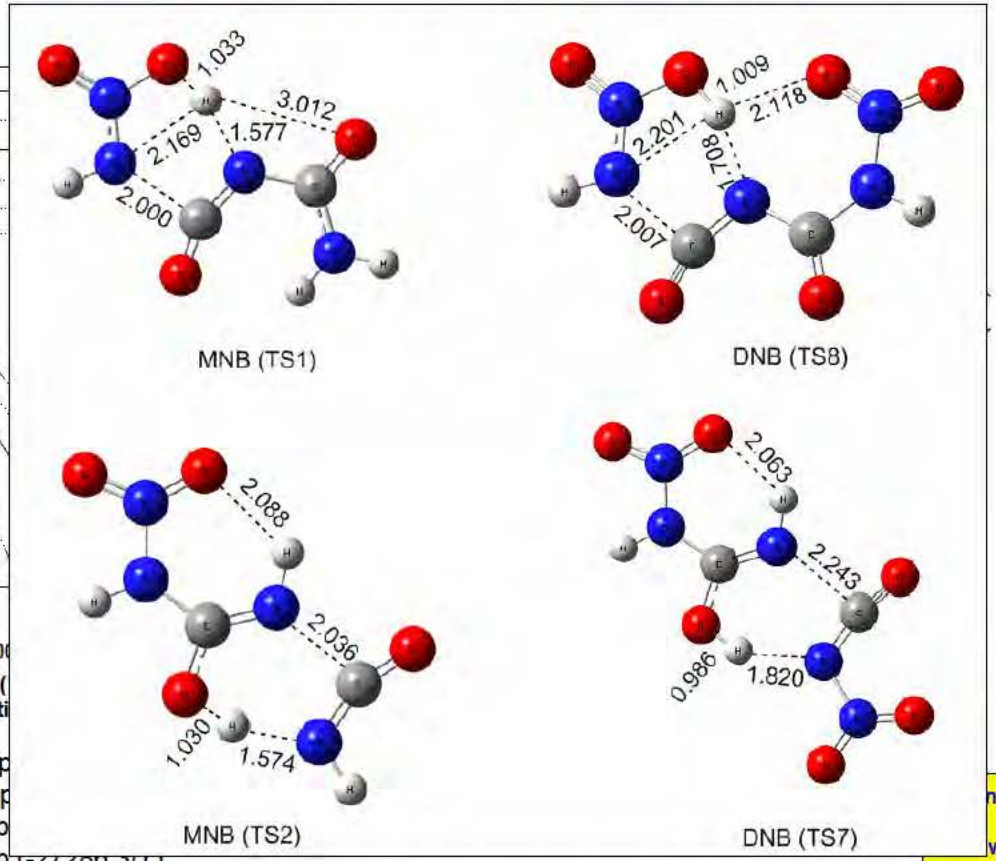


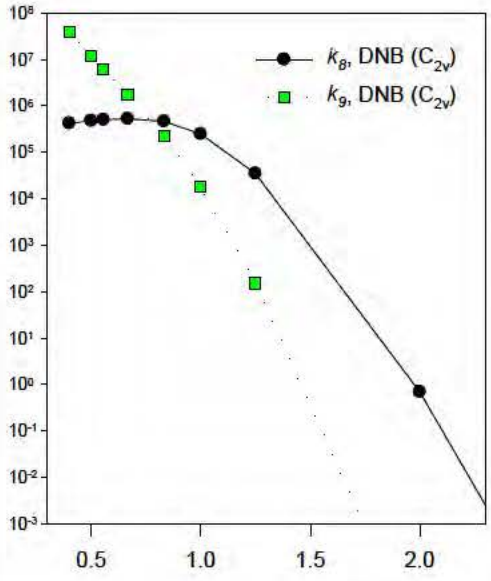
Ab initio Kinetics of DNB Thermal Decomposition



High-pressure rate limit for DNB (primary thermal decompositi

$k_{6,\infty} = 3.22 \times 10^{14}\, T^{-0.289}$ exp
$k_{7,\infty} = 8.49 \times 10^{16}\, T^{-0.882}$ exp
$k_{8,\infty} = 9.72 \times 10^{13}\, T^{-0.248}$ exp
$k_{9,\infty} = 9.96 \times 10^{23}\, T^{-2.205}$ exp (-27286.3/T)





Rate coefficients at pressure of 1 atm for DNB (C_{2v}) primary thermal decomposition channels

ng pressure dependences observed

w 1200 K, HNN(O)OH elimination dominates

Below 1500 K, HNN(O)OH elimination dominates from DNB (C_{2v})

Above 1500 K, NO_2 elimination dominates from DNB (C_{2v})

Similar trend seen in Liu *et al.*, 2011, and good agreement above 1500 K

k_8 for HNN(O)OH elimination from DNB is much larger than k_1 for HNN(O)OH from MNB below 800 K

Consistent with TS1 (and TS3) energy higher than TS8 (Also, TS2 higher than TS7)

TS8 is stabilized by additional intramolecular H-bonding (Also, TS7 is a late transition state)

DNB is less stable than MNB

Present quantitative interpretations are consistent with experimental work of Gieth *et al.* 2004

Conclusions & Acknowledgements

- N_2H_3 + NO_2 addition reaction is fast
  - trans-N_2H_2 + trans-HONO main products
- PES surface characterized
  - Calculated reaction rate coefficients in agreement with experiments
- MNB & DNB stabilized via 6-member-ring moieties involving intramolecular H-bonding
  - Solid state conformers have smallest dipole moment
- Energy barriers and endothermicities at the M06-2X/aug-cc-pVTZ level of theory show remarkable agreement with the values obtained from RCCSD(T)/cc-pV∞Z//M06-2X/aug-cc-pVTZ computations
  - Former level of theory should be applicable to larger analogous systems
- MNB decomposition initiated by the elimination of HNCO and HNN(O)OH, the latter is also released in DNB (C_{2v}) decomposition
- Energy barrier for HNN(O)OH elimination in DNB is 6.60 kcal/mol lower than that in MNB due to an extra hydrogen bond in the transition state for the former
  - DNB less stable than MNB (as previously shown by experiments)

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